The adhesive properties of viscoelastic liquid films

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1. Introduction
The adhesion of poly(dimethylsiloxane) (PDMS) liquid films was measured using colloidal probe atomic force microscopy (AFM). Molecular weights in the range 7 - 250 kg/mol were used, which corresponded to Newtonian and non-Newtonian liquids with zero-shear rate viscosities in the range 10^{-1} - 10^3 Pa.s.

Fixed end retraction velocities in the range 10^2 - 10^4 nm/s were used, with the colloidal probe approached to within 10 nm of the substrate onto which the PDMS film was spin coated. Film thicknesses in the range 0.2 – 2.0 μm were investigated. The SiO_2 colloidal probes exhibited radii in the range 2.5 – 6.0 μm.

2. Theory and Experimental
A model was derived for calculating the time-dependent adhesive force during the separation of a liquid junction; this comprised:
(i) the cantilever, which is the compliant load measuring element;
(ii) a colloidal probe at the cantilever free end, which contacts the sample;
(iii) physical properties of the PDMS liquid film, including surface tension, film thickness, and contact radius;
(iv) rheological properties of the PDMS liquid, including non-linear viscoelasticity, described using a generalised Maxwell model.

The capillary number, Ca, was used to allow meaningful comparison of the wide range of viscosities and velocities investigated.

3. Results: Rheometry
- Critical entanglement molecular weight for PDMS liquids is 34 kg/mol.
- Non-Newtonian PDMS liquids required between 1-4 elements for successful fitting to the generalised Maxwell model, depending on molecular weight.
- Master curves for storage and loss modulus permitted extrapolation for frequencies which were not experimentally accessible.
- Measurable strain dependence for PDMS liquids with molecular weights in excess of 60 kg/mol.
- Two-parameter damping function used for fitting strain dependence data.

4. Results: Atomic Force Microscopy
- Incorporating the rheological properties of PDMS liquids was crucial to constructing an accurate model, including capillary and viscous forces.
- Beam mechanics, including inertia and acceleration, also present in the model.
- Peak force dominated by capillary contribution for Ca < 10^{-3}.
- For Ca > 10^{-3}, peak force increases with increasing Ca due to viscous contribution.
- Good agreement between experimental data and simulation for 10^{-7} < Ca < 10^{-1}.
- Contribution from stress overshoot negligibly small due to low velocities of AFM.

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